

The Determination of Lead, Manganese and Mercury by Means of Periodate

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE UNIVERSITY OF MICHIGAN

By
Joseph John Thompson

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CONTENTS

	PAGE
Qualitative Tests for Periodate and Iodate in the Presence of Each Other.....	1
The Periodates of Lead.....	3
Quantitative Determination of Lead as Periodate.....	9
Volumetric Determination of Manganese after Oxidation by Periodate.....	12
Volumetric and Gravimetric Determination of Mercury as Periodate.....	18
The Action of Periodate on Salts of Various Metals.....	22



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Qualitative Tests for Periodate and Iodate in the Presence of Each Other

In the course of an investigation of the action of a soluble periodate on the salts of various metals a few metals were found which formed periodates insoluble even in solutions which were quite strongly acid. Since the corresponding iodates were soluble it was found possible by this means to precipitate a very small amount of periodate in the presence of a large amount of iodate. Bismuth was chosen because its periodate is least soluble and can be obtained in a fairly dense and easily filterable form.

Experimental

One gram of bismuth nitrate and 50 mg. of sodium iodate were dissolved in 30 cc. of water containing sufficient perchloric acid to maintain a clear solution. This was added to 5 cc. of water containing 0.1 mg. of periodate ion. Immediately the solution became opalescent due to the precipitation of the very insoluble bismuth periodate. If more than 50 mg. of iodate ion was present, too much acid was required to keep the bismuth iodate from precipitating, thereby diminishing the sensitivity of the test because of the increased solubility of the bismuth periodate. To detect smaller proportions of periodate, 5 g. of sodium iodate and various amounts of sodium periodate were dissolved in 100 cc. of water, which was acidified with 1 cc. of nitric acid, sp. gr. 1.42. Then 12 g. of barium nitrate was added to precipitate most of the iodate. This was filtered off and the filtrate tested for periodate by adding

bismuth nitrate. It was found that 0.6 mg. of periodate ion could be detected in 5 g. of iodate ion in a volume of 100 cc.

It was not possible to detect the presence of small amounts of iodate in periodate by precipitating the periodate with bismuth and testing the filtrate for iodate, because small quantities are completely adsorbed by the bismuth periodate. However, it was found that 1.5 mg. of iodate ion could be detected in the presence of 5 g. of periodate in a volume of 25 cc., if most of the periodate was first precipitated as potassium metaperiodate, KIO_4 , by adding an excess of potassium nitrate. This was shown by dissolving 5 g. of sodium periodate and 1.5 g. of sodium iodate in 100 cc. of water and adding 10 g. of potassium nitrate to the boiling solution, which was then allowed to evaporate at 80° to 25 cc. The solution was cooled in ice, filtered and washed with ice water. The cold filtrate was slightly acidified with nitric acid and tested for iodate by adding 5 cc. of 0.5 *M* silver nitrate. An opalescence appeared due to the formation of silver iodate. This was the limit of sensitivity.

All ions which are precipitated by silver interfere in the detection of iodate. Reducing ions react with periodate while chloride, bromide and phosphate ions interfere with its detection because they precipitate bismuth salts. The procedures given above are suitable for testing reagent iodate and periodate.

Summary

Six tenths of a milligram of periodate ion in the presence of 5 g. of iodate ion can be detected in 100 cc. of solution by first removing most of the iodate with barium nitrate, and then precipitating the periodate with bismuth nitrate.

One and five-tenths milligram of iodate ion can be detected in the presence of 5 g. of periodate ion in 25 cc. of solution by first removing most of the periodate as the insoluble potassium periodate, KIO_4 , and then precipitating the iodate with silver nitrate.

Periodates of Lead

The literature of the periodates of lead is confusing. Not less than seven salts are described. An investigation of this subject resulted in the identification of only two salts, namely, triplumbous paraperiodate, $\text{Pb}_3\text{H}_4(\text{IO}_6)_2$, and the mesoperiodate, $\text{Pb}_3(\text{IO}_5)_2$. The former might also be considered as the mesoperiodate dihydrate, $\text{Pb}_3(\text{IO}_5)_2 \cdot 2\text{H}_2\text{O}$, but this is improbable for reasons given later.

A study of the periodates of lead involved: (a) the preparation of a few soluble periodates, (b) methods of analysis of the lead periodates.

Preparation of Soluble Periodates.—Sodium metaperiodate, NaIO_4 , was prepared by dissolving trisodium paraperiodate, $\text{Na}_3\text{H}_2\text{IO}_6$, in a 15% nitric acid solution and evaporating until crystals of sodium metaperiodate formed. The trisodium paraperiodate was obtained by first oxidizing iodine to iodate by means of sodium chlorate and subsequently oxidizing the iodate to periodate in an alkaline solution with chlorine gas. The potassium salt, KIO_4 , was obtained directly by the latter process. Periodic acid, H_5IO_6 or $\text{HIO}_4 \cdot 2\text{H}_2\text{O}$, was obtained by treating barium periodate, $\text{Ba}_3\text{H}_4(\text{IO}_6)_2$, with concentrated nitric acid, filtering off the barium nitrate and removing the excess of nitric acid by vacuum distillation. The barium salt was prepared by treating trisodium paraperiodate with barium nitrate. Periodic acid can also be prepared electrolytically.¹

(1) Willard and Ralston, *Trans. Am. Electrochem. Soc.*, **62**, 249 (1932).

Analysis of the Periodates of Lead.—Two methods for analyzing the precipitated lead periodates were employed. The procedures were as follows.

(1) The lead periodate was treated with 10 cc. of sulfuric acid (sp. gr. 1.84) and heated until it was converted completely to lead sulfate and periodic acid. It was then diluted to 300 cc. and cooled. The lead sulfate was filtered onto a Gooch crucible, washed with dilute sulfuric acid and ignited in an electric muffle at 500° for two hours. The filtrate was neutralized with sodium hydroxide, then a solution containing 9 g. of borax and 9 g. of boric acid was added, and finally 5 g. of potassium iodide. The iodine liberated was titrated with 0.1 *N* arsenite.²

(2) The periodate was treated in the same manner as described in (1) except that after filtering off and washing the lead sulfate, the periodic acid in the filtrate was reduced with sulfur dioxide and the iodine determined gravimetrically as silver iodide.

Experimental

A study was made of the salts obtained by varying the concentration of lead, the acidity and temperature. Experiments were made by precipitating the periodate from: (A) hot and cold concentrated neutral solutions of a lead salt; (B) hot and cold dilute neutral solutions of a lead salt; (C) acid solutions.

Lead Periodate (A) from Concentrated Neutral Solutions.—To study the type of salt formed from a concentrated solution, 25 g. of c. p. lead nitrate was dissolved in 100 cc. of water and the lead periodate precipitated at 25° by the slow addition of 100 cc. of water containing 17 g. of sodium metaperiodate, NaIO_4 , with continuous mechanical stirring. A white granular precipitate was formed which, after filtering, was twice suspended in fresh water and washed thoroughly by decantation, using ice were dependent upon the temperature and the time of

(2) E. Müller and O. Friedberger, *Ber.*, **35**, 2655 (1902).

water, then filtered on a fritted glass filter, washed and dried over phosphorus pentoxide. The dry salt remained white and was crystalline, as shown by the microphotograph in Fig. 1.

When the solution was maintained at 100° instead of 25°, a yellow-orange crystalline precipitate of impure triplumbous paraperiodate, $\text{Pb}_3\text{H}_4(\text{IO}_6)_2$, was formed. The analyses of the salts precipitated at the different temperatures are given in Table I.

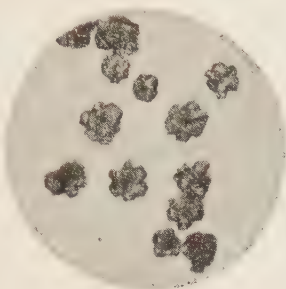


Fig. 1.—Lead periodate from cold, concentrated neutral solutions.

Lead Periodate (B) from Dilute Neutral Solutions.—A study of the precipitates from dilute solutions of a lead salt was made by dissolving 25 g. of lead nitrate in 500 cc. of water and precipitating the lead at 25° by the slow addition of 17 g. of sodium metaperiodate in 200 cc. of water. A white crystalline precipitate was formed. This was filtered, washed and dried over phosphorus pentoxide. The crystals which consist of thin plates are shown in Fig. 2.

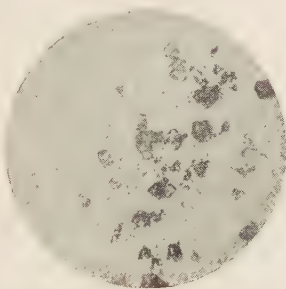


Fig. 2.—Lead periodate from cold, dilute neutral solution.

When precipitated at 100°, the crystals were light orange in color. Analyses of the salts dried over phosphorus pentoxide are shown in Table I. In both cases triplumbous paraperiodate was formed.

Lead Periodate (C) from Acid Solutions.—When 25 g. of lead nitrate was dissolved in 100 cc. of 0.8 *N* nitric acid and the lead precipitated at 100° by the slow addition of 17 g. of sodium metaperiodate in 100 cc. of water, the first 10 cc. of the periodate solution did not give a permanent precipitate, but as more was added a white flocculent precipitate formed which gradually changed to a very light cream-colored, fine, crystalline salt that settled rapidly. The salt was filtered, washed with 150 cc. of hot 1% nitric acid, transferred to a beaker, and washed by decantation, using cold 1% nitric acid, filtered on a fritted glass filter, finally washed with 100 cc. of ice water, and dried over phosphorus pentoxide. Results of analyses in Table I show that impure $\text{Pb}_3\text{H}_4(\text{IO}_6)_2$ was formed.

In the mother liquor white crystals formed upon cooling. These were filtered, washed, dried over phosphorus

pentoxide and analyzed. The analyses showed that the salt was impure $\text{Pb}_3\text{H}_4(\text{IO}_6)_2$.

Further study in hot and cold acidified solutions resulted in the preparation of pure triplumbous paraperiodate. It was found that when the acidity was approximately 0.006 to 0.1 *N* with nitric acid, or 0.9 *N* with acetic acid, the pure salt was obtained. Results are shown in Table I. Microphotographs of the different crystal structures are shown in Fig. 3.

TABLE I
ANALYSES OF LEAD PERIODATE (A), (B) AND (C)

Sam- ple	% PbO Found		% I_2O_7 Found		Temp. of soln., °C.	Normality of acid	Method of analysis
(A)	61.81	61.82	34.17	34.24	25		1
	61.88	61.77	33.86	34.04	25		2
(A)	62.03	62.29	33.63	33.38	100		1
	62.15	62.31	33.68	33.62	100		2
(B)	61.87	61.86	33.80	33.82	25		1
	61.98	61.93	33.91	34.09	25		2
(B)	62.01	62.02	33.73	33.69	100		1
	62.41	62.38	33.87	33.69	100		2
(C)	61.93	62.11	33.87	33.90	100	0.8 <i>N</i> Nitric acid	1
	62.30	62.21	33.85	33.89	25	0.8 <i>N</i> Nitric acid	1
(C)	62.35	62.32	34.13	34.09	100	0.16 <i>N</i> Nitric acid	2
	62.47	62.42	33.90	33.97	25		2
(C)	62.46	62.38	34.10	34.07	100	0.047 <i>N</i> Nitric acid	2
(C)	62.05	62.23	34.12	34.13	100	0.88 <i>N</i> Acetic acid	2
	62.47	62.56	34.14	34.16	25		2

The theoretical for $\text{Pb}_3\text{H}_4(\text{IO}_6)_2$ is 62.49% PbO and 34.13% I_2O_7 .

The Behavior of Triplumbous Paraperiodate on Heating.—Kimmins stated that the para salt was converted into the meso form, $\text{Pb}_3(\text{IO}_5)_2$, when it was heated for four hours at 275°. In an effort to prepare the meso salt, pure $\text{Pb}_3\text{H}_4(\text{IO}_6)_2$ was heated at 275° for four hours and then analyzed by Method 2. The results indicate that the para salt was converted essentially into the meso form, but qualitative tests showed that in its conversion a portion had undergone decomposition with the formation of some lead iodate. PbO found, 64.44, 64.46, 64.55, calcd. for $\text{Pb}_3(\text{IO}_5)_2$, 64.68%. I_2O_7 found, 35.39, 35.39, 35.35, calcd., 35.34%.

When pure or impure triplumbous paraperiodate was heated above 130°, the formation of anhydrous meso salt caused a change in color to a dark brick red. The intensity of the color change and the amount of water lost

heating. If the brick red salt was pulverized very finely, it became orange colored.

When the pure paraperiodate was converted into the anhydrous meso salt, the loss in weight corresponding to water was always too great, varying from 3.49 to 3.61% compared to the theoretical value of 3.38%; therefore the temperature of heating was varied from 130 to 275°, and the time from three minutes to six hours. Volumetric analyses of the heated samples showed that when the temperature was high enough to remove all the water there was a loss of oxygen with consequent formation of iodate.

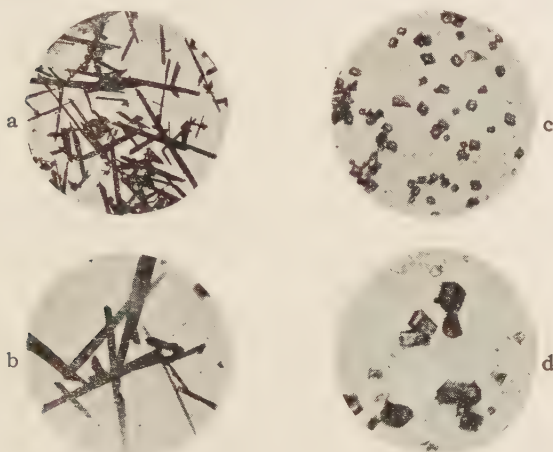


Fig. 3.—Lead periodate from acid solutions: a, 0.8 *N* nitric acid, 100°, no precipitate formed until cooled; b, 0.8 *N* nitric acid, 100°, no precipitate formed until cooled; c, 0.047 *N* nitric acid, 100°; d, 0.047 *N* nitric acid, 100°.

It is believed that the salt before heating is the paraperiodate and not the mesoperiodate dihydrate for two reasons: (1) the water is retained up to 130°; (2) the anhydrous meso salt when kept under water for fifteen hours and again dried at 110° is found to have absorbed only 5% of the water lost.

Summary

1. Lead periodate was precipitated under varying conditions of acidity, temperature and concentration, only triplumbous paraperiodate, $\text{Pb}_3\text{H}_4(\text{IO}_6)_2$, being formed, although crystals of very different types and colors were obtained. It was pure only when precipitated from 0.006 to 0.1 *N* nitric acid or 0.9 *N* acetic acid solutions. This

salt might also have the formula $\text{Pb}_3(\text{IO}_6)_2 \cdot 2\text{H}_2\text{O}$ but the para formula is more probable because the water is retained up to 130° and is not taken up by the anhydrous salt.

2. When the para salt was heated to 275° for fifteen minutes it was converted into triplumbous mesoperiodate, $\text{Pb}_3(\text{IO}_6)_2$, with slight reduction to iodate.

3. None of the other periodates of lead described in the literature could be prepared.

Quantitative Determination of Lead as Periodate

IT WAS found that pure triplumbic paraperiodate was sufficiently insoluble in very dilute acid solutions to make possible its use in the volumetric and gravimetric determination of lead.

EXPERIMENTAL

Weighed samples of Mallinckrodt's reagent-quality lead or Kahlbaum's sheet lead were dissolved in nitric acid and evaporated to dryness. The dry salt was then dissolved in 200 cc. of 0.025 *N* nitric acid and the lead precipitated at 100° C. by the slow addition of 2 grams of sodium periodate, NaIO₄, dissolved in 50 cc. of water. When the amount of lead was very small, no precipitate formed until after 1 cc. of the periodate solution had been added. When this occurred, it was necessary to decrease the acidity to 0.006 *N*; otherwise the precipitate did not have the theoretical composition. After the periodate was added, the solution was cooled in ice water and the cold solution stirred for 0.5 hour, because supersaturation was very pronounced. The lead periodate was filtered on a porcelain filtering crucible, washed with ice water, and dried for 2 hours at 110° C. It was then weighed as Pb₃H₄(IO₆)₂. Results of analyses are shown in Table I.

To determine the lead periodate volumetrically the method of Andrews (1, 2) was used, because the best solvent for the salt is concentrated hydrochloric acid. The equation for the reaction can be expressed as follows:



If arsenious acid is present in excess, all the chlorine will react with it to form arsenic acid. The excess arsenious acid can then be titrated with iodate, using chloroform as indicator.

The precipitate was filtered into a Gooch crucible, the bottom of which was covered with a filter-paper disk, washed thoroughly, and transferred to a 150-cc. conical flask. An excess of arsenious oxide previously dissolved in a concentrated solution of sodium

TABLE I. GRAVIMETRIC DETERMINATION OF LEAD AS $\text{Pb}_3\text{H}_4(\text{IO}_6)_2$

LEAD TAKEN	LEAD FOUND	ERROR
<i>Gram</i>	<i>Gram</i>	<i>Mg.</i>
0.7001	0.7001	± 0.0
0.6953	0.6954	+0.1
0.6028	0.6025	-0.3
0.5596	0.5596	± 0.0
0.5591	0.5588	-0.3
0.5553	0.5552	-0.1
0.3853	0.3852	-0.1
0.1145	0.1147	+0.2
0.1121	0.1122	+0.1
0.0735	0.0734	-0.1

TABLE II. VOLUMETRIC DETERMINATION OF LEAD AS $\text{Pb}_3\text{H}_4(\text{IO}_6)_2$

LEAD TAKEN	LEAD FOUND	ERROR	As_2O_3 ADDED
<i>Gram</i>	<i>Gram</i>	<i>Mg.</i>	<i>Gram</i>
0.5920	0.5921	+0.1	0.7111
0.4896	0.4895	-0.1	0.7447
0.3069	0.3067	-0.2	0.4006
0.2920	0.2920	0.0	0.4135
0.2060	0.2063	+0.3	0.3297
0.1554	0.1557	+0.3	0.2320
0.1103	0.1101	-0.2	0.1299
0.1037	0.1035	-0.2	0.1271
0.1001	0.0999	-0.2	0.1125
0.0653	0.0655	+0.2	0.1005
0.0496	0.0494	-0.2	0.2116

hydroxide or a suitable volume of standard arsenite solution was added to the flask. Concentrated hydrochloric acid was slowly added to the cold solution, the flask being agitated until all the lead periodate dissolved, which required 35 to 40 cc., and the solution was titrated with 0.1 *N* potassium iodate until it was a light brown in color. A little chloroform was then added and the titration completed. The results of the volumetric determination of lead as periodate are shown in Table II.

SEPARATION OF LEAD AS PERIODATE FROM OTHER METALS

The possibility of separating lead as $\text{Pb}_3\text{H}_4(\text{IO}_6)_2$ from other metals is rather limited, since most metals form periodates which are insoluble in low acid concentrations. The results of the separation of lead as periodate from other metals are shown in Table III. The lead was determined volumetrically.

TABLE III. SEPARATION OF LEAD AS $\text{Pb}_3\text{H}_4(\text{IO}_6)_2$

LEAD TAKEN	LEAD FOUND	ERROR	OTHER METALS PRESENT
<i>Gram</i>	<i>Gram</i>	<i>Mg.</i>	<i>Gram</i>
0.6771	0.6778	+0.7	0.4 Ni
0.5643	0.5709	+6.6	0.26 Cu ^a
0.5163	0.5160	-0.3	0.05 Cu
0.5375	0.5374	-0.1	0.21 Al
0.5161	0.5163	+0.2	0.22 Zn
0.5944	0.5971	+2.7	0.37 Cd ^a
0.5570	0.5575	+0.5	0.07 Cd
0.5438	0.5440	+0.2	0.2 Ca
0.5567	0.5563	-0.4	0.2 Mg

^a Double precipitation would obviously have been satisfactory.

SUMMARY

Lead can be separated from nickel, copper, zinc, cadmium, aluminum, calcium, and magnesium by precipitating it as $\text{Pb}_3\text{H}_4(\text{IO}_6)_2$ from 0.025 *N* nitric acid solution by the addition

of sodium periodate. The precipitate can be weighed or determined volumetrically by dissolving it in concentrated hydrochloric acid containing an excess of standard arsenite, and titrating the excess with standard iodate, using chloroform as indicator.

LITERATURE CITED

- (1) Andrews, L. W., *J. Am. Chem. Soc.*, 25, 756 (1903).
- (2) Jamieson, G. S., "Volumetric Iodate Methods," Chemical Catalog Co., Inc., N. Y., 1926.

Volumetric Determination of Manganese after Oxidation by Periodate

Manganese up to 30 mg. can be determined by oxidation to permanganate with periodate in either phosphoric or sulfuric acid solution, removal of excess periodate by precipitation as mercuric salt, and reduction of the permanganate by standard ferrous sulfate. The reaction goes best in a phosphoric acid solution, in which case less than a milligram of chromium does not interfere. Cobalt, cerium, and chloride must be absent.

WILLARD and Greathouse (4) have shown that manganese can be determined colorimetrically by oxidation to permanganate with a small excess of periodate. The solution thus obtained is stable for weeks, a fact confirmed by others (3). It seemed desirable, therefore, to make this the basis of a volumetric method by removing the excess of periodate. This was accomplished by precipitation as mercuric periodate, after which the permanganate was titrated by adding excess of standard ferrous sulfate and back titrating with permanganate. Although bismuth periodate is the least soluble of all, its presence caused certain errors which made its use for this purpose impossible.

Precipitation of Periodate as Bismuth Salt

A known volume of standard permanganate was reduced with ferrous sulfate in a dilute sulfuric acid solution, and the manganous salt was then oxidized to permanganate by adding 0.3 gram of sodium metaperiodate, NaIO_4 , and boiling gently for 15 minutes. After cooling to room temperature, the excess periodate was precipitated by the addition of bismuth perchlorate, as a white, voluminous precipitate of bismuth periodate. The solution was immediately titrated with standard ferrous sulfate. To make the end point more distinct in the presence of the precipitate, alphanaphthylamine (Erioglaucine A) (2) was added just before the end point. Too little ferrous sulfate was always used, showing that some permanganate had been reduced, because other experiments proved that oxidation was complete. The surprising fact was that in the presence of iodate some of the permanganate was used in the oxidation of bismuth. In the presence of bismuth periodate only, no such error occurred. Both bismuth and iodate are necessarily present because the latter is formed by reduction of the periodate by manganous ion (4). It could not be completely removed by precipitation as silver iodate. If standard permanganate to which as much as 0.6 gram of sodium periodate had been added was treated with a bismuth salt, and, without filtering, titrated with ferrous sulfate, accurate results were obtained. If, however, excess of the latter was added and back titrated with permanganate, the results indicated that the excess of ferrous salt was slowly oxidized by the precipitate of bismuth periodate even in cold solution.

There are, therefore, two errors to be considered: oxidation of the excess reducing agent by iodate or insoluble bismuth periodate, and oxidation of bismuth. Of the possible volumetric reducing agents, vanadyl sulfate and ferrous sulfate were slowly oxidized by bismuth periodate, but oxalate and hydrogen peroxide were not affected. On the other hand, the former were not oxidized by the low concentration of iodate, but the two latter were oxidized. The use of bismuth as a precipitant, therefore, had to be abandoned.

Precipitation of Periodate as Mercuric Salt

It was found that periodate could be completely precipitated as the mercuric salt, $\text{Hg}_5(\text{IO}_6)_2$. Although more soluble than the bismuth salt, it is still sufficiently insoluble even in the concentration of acid used for the oxidation of manganese, provided a large excess of mercuric ion is present. The mercuric salt has a very decided advantage in that it is much more easily filtered. There is also no possibility of further oxidation of the mercury by permanganate. Experiments showed that amounts of manganese up to 30 mg. could be accurately determined by oxidation to permanganate in a solution containing either phosphoric, sulfuric, or phos-

phoric and sulfuric acids. There was no blank correction to be applied. In this respect there is a slight advantage over the bismuthate method (1). Iron ores can be quickly dissolved in phosphoric acid and this method applied directly to the solution, but this is not possible with bismuthate.

Table I—Effect of Chromium on Determination of Manganese

MATERIAL USED	ACID PRESENT	AP- PROX.	CHRO-	MANGANESE	
		WT. OF	MIUM	Present	Found
		Grams	Mg.	%	%
B. S. Steel, No. 10c	Phosphoric	1.1	4.0	1.13	1.160
B. S. Steel, No. 10c	Phosphoric	1.0	3.0	1.13	1.153
B. S. Steel, No. 10c	Phosphoric	1.0	2.0	1.13	1.148
B. S. Steel, No. 10c	Sulfuric	1.3	2.0	1.13	1.232
B. S. Steel, No. 10c	Phosphoric	1.0	1.5	1.13	1.143
B. S. Steel, No. 10c	Phosphoric	1.0	1.0	1.13	1.138
B. S. Steel, No. 10c	Phosphoric	1.0	0.5	1.13	1.139
B. S. CrNi Steel, No. 32b	Phosphoric	1.14	7.3	0.624	0.661
B. S. CrNi Steel, No. 32b	Phosphoric	1.04	6.6	0.624	0.664
B. S. CrNi Steel, No. 32b	Phosphoric	1.18	7.6	0.624	0.749
B. S. CrNi Steel, No. 32b	Phosphoric	1.20	7.7	0.624	0.686

Experiments using standard permanganate were carried out to determine the accuracy of the method. Samples of 25 to 40 cc. of 0.05 *N* permanganate were reduced with ferrous sulfate in a solution containing, in a volume of 100 cc., about 10 to 15 cc. of 85 per cent phosphoric acid, or mixtures of 3 or 4 cc. of phosphoric acid with 5 or 4 cc. of concentrated sulfuric acid, and oxidized by adding 0.3 to 0.5 gram of sodium or potassium periodate and heating just to boiling for 15 minutes. The solution was cooled to room temperature, diluted to 150 cc., and 2 to 5 grams of mercuric nitrate, $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, dissolved in a little water, were added to precipitate the excess periodate and nearly all of the iodate. The solution was filtered into an excess of 0.05 *N* ferrous sulfate through an asbestos mat 3 to 4 mm. thick on a 9-cm. No. 17G sintered-glass filtering funnel. A Büchner funnel would doubtless be almost as satisfactory. The precipitate of mercuric periodate was washed four times with water, and the excess of ferrous sulfate was titrated back with standard permanganate. The results obtained were the same within 0.01 cc. as in the direct titration of the ferrous sulfate with permanganate. When chromium was present, it was found that in the presence of sulfuric acid about 60 per cent of it was oxidized when the content was about 1.5 mg., thereby giving high results for manganese. However, this tendency is very much minimized in phosphoric acid solutions, so that an accurate determination of manganese can be made in the presence of 1 mg. of chromium. Because of the difficulty in washing out all the permanganic acid from very large precipitates of mercuric periodate, only 0.3 gram of sodium or potassium periodate should be used for 15 mg. or less of manganese. Accurate results can be obtained, however, with as much as 30 mg. of manganese, using, in this case, 0.5 gram of periodate. With

larger amounts such voluminous precipitates are formed that all the permanganic acid cannot be removed by washing. Instead of the metaperiodate, the paraperiodate, $\text{Na}_3\text{H}_2\text{IO}_6$, may be used. Manganese is more readily oxidized and the permanganic acid formed is more stable in a phosphoric acid solution, so that this acid is desirable when considerable amounts of manganese are present.

The concentration of acid may vary within wide limits as far as oxidation of manganese is concerned, although with large amounts of the latter, manganese dioxide may form unless phosphoric acid is present. A fairly high concentration of acid increases the rate of oxidation. The solubility of mercuric periodate, however, is increased under these conditions, so that it is advisable to dilute the solution before removing the excess of periodate. Concentrations not greater than 5 cc. of sulfuric acid, sp. gr. 1.83, or 15 cc. of 85 per cent phosphoric acid per 100 cc. are recommended. Mixtures of the two acids are desirable, because the mercuric periodate is more crystalline in the presence of sulfuric acid, and without some phosphoric acid, manganese dioxide may form.

The weight of mercuric nitrate required for complete precipitation of periodate varies from 5 grams with 5 cc. of sulfuric acid to 2 grams with 15 cc. of phosphoric acid per 100 cc.

Titration of the permanganic acid with arsenite instead of ferrous sulfate is impossible because of an indefinite end point.

Chloride must be absent. Cobalt interferes as in the bismuthate method (1). When periodate is added to a solution of cobaltous sulfate, the solution becomes dark brown, owing to oxidation of the cobaltous salt. In steel containing 1.13 per cent of manganese and 0.5 per cent of cobalt, 1.32 per cent of manganese was obtained. Cerium also interferes because it is oxidized to a ceric salt.

Procedure for Steel or Iron Free from Chromium

Dissolve 1 gram of steel containing not more than 0.15 mg. of chromium in 4 cc. of concentrated sulfuric acid and 25 cc. of water. To the hot solution, add, cautiously, 1 cc. or more of concentrated nitric acid to oxidize the ferrous iron and carbonaceous matter, and boil to remove nitrous fumes. Any graphite present will do no harm and will be filtered out later. Dilute to 50 or 75 cc., add 3 cc. of 85 per cent phosphoric acid (or an equivalent amount of more dilute acid) and 0.3 gram of sodium or potassium periodate. Boil gently for 15 minutes to oxidize the manganese, dilute to 150 cc., cool to room temperature, and add slowly, with constant stirring, 4 or 5 grams of mercuric nitrate ($\text{Hg}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$) dissolved in a little water. Filter immediately through a fairly large asbestos filter into an excess of standard

ferrous sulfate, wash with cold water four or five times, and titrate back with standard permanganate.

Procedure for Steel or Iron Containing Not Over 0.1 Per Cent of Chromium

Dissolve 1 gram in a mixture of 15 cc. of water and 15 cc. of 85 per cent phosphoric acid. Oxidize the ferrous iron and carbonaceous matter by adding carefully to the hot solution 1 or 2 cc. of concentrated nitric acid, and boil to remove nitrous fumes. Dilute to 100 cc., add 0.3 gram of sodium or potassium periodate, boil gently 15 minutes to oxidize the manganese, dilute to 150 cc., and cool to room temperature. Precipitate the periodate by adding slowly, with constant stirring, 2 to 3 grams of mercuric nitrate dissolved in a little water, and filter immediately through a fairly large asbestos filter into excess of standard ferrous sulfate containing 10 cc. of 50 per cent sulfuric acid to prevent precipitation of mercuric phosphate. Wash with cold water four or five times and titrate back the filtrate and washings with standard permanganate. The filtration will be slower than when sulfuric acid is present during precipitation, but the time required, including washing, should not be more than 3 minutes. The effect of chromium with and without phosphoric acid is shown in Table I.

Procedure for Iron Ore and Other Oxide Ores

Place 1 gram in a 250-cc. Pyrex beaker, and add 15 cc. of 85 per cent phosphoric acid and a few drops of concentrated sulfuric acid. Stir until all the ore is free from the bottom of the beaker, cover, and heat until fumes of sulfuric acid are given off, taking care that it does not froth over or cake on the bottom. If the ore is not dissolved by this time, keep it hot for a longer time, stirring occasionally, but not allowing the temperature to rise, because the beaker would be attacked. Cool until the mass begins to be viscous, then add quickly 100 cc. of water, and heat. Everything should dissolve except some gelatinous silica. From here on the procedure is the same as for steel containing 0.1 per cent of chromium.

Procedure for Bronze

Dissolve 1 gram in a mixture of 3 cc. of concentrated nitric acid, 10 cc. of 85 per cent phosphoric acid, and about 7 or 8 cc. of water. Then dilute to 50 or 75 cc. and proceed as above. Owing to the deep blue color of the copper salt, the back titration with permanganate is conveniently carried out electrometrically or by use of alphanurine indicator (2).

Note—If the amount of manganese is between 15 and 30 mg., the amount of periodate in the above procedures should be increased to 0.5 gram.

Results obtained by this method with different materials are shown in Table II. In all cases phosphoric acid was

used with the sulfuric to prevent formation of manganese dioxide.

Table II—Determination of Manganese in Various Materials

MATERIAL ANALYZED	ACID USED	AP- PROX. CHRO- WT. OF PRES- MUM		MANGANESE	
		SAMPLE	ENT	Present	Found
				%	%
B. S. Steel, No. 10c	Phosphoric	1.06	0.01	1.13	1.136
B. S. Steel, No. 10c	Phosphoric	1.03	0.01	1.13	1.132
B. S. Steel, No. 10c	Sulfuric	1.29	0.01	1.13	1.138
B. S. Steel, No. 10c	Sulfuric	1.01	0.01	1.13	1.139
B. S. Cast Iron, No. 4c	Phosphoric	1.04	0.016	0.897	0.890
B. S. Cast Iron, No. 4c	Phosphoric	1.18	0.016	0.897	0.894
B. S. Cast Iron, No. 4c	Sulfuric	1.14	0.016	0.897	0.898
B. S. Cast Iron, No. 4c	Sulfuric	1.13	0.016	0.897	0.912
B. S. Steel, No. 21b	Phosphoric	1.26	0.021	0.564	0.570
B. S. Steel, No. 21b	Phosphoric	1.12	0.021	0.564	0.562
B. S. Steel, No. 16b	Phosphoric	1.10	0.007	0.381	0.389
B. S. Steel, No. 16b	Phosphoric	1.24	0.007	0.381	0.388
B. S. Steel, No. 16b	Sulfuric	1.02	0.007	0.381	0.390
B. S. Steel, No. 16b	Sulfuric	1.22	0.007	0.381	0.392
Steel A	Phosphoric	1.47 ^a	0.065	1.99	1.99
Steel A	Phosphoric	1.46 ^a	0.065	1.99	1.98
Steel A	Sulfuric	0.49	0.065	1.99	2.02
Steel A	Sulfuric	0.43	0.065	1.99	2.00
B. S. Mn Bronze, No. 62	Phosphoric	0.69	...	1.59	1.61
B. S. Mn Bronze, No. 62	Phosphoric	0.62	...	1.59	1.64
B. S. Norrie Iron Ore, No. 28	Phosphoric	1.00	...	0.465	0.446
B. S. Norrie Iron Ore, No. 28	Phosphoric	1.09	...	0.465	0.447
B. S. Bauxite, No. 69	Phosphoric	1.27	...	0.426	0.421
B. S. Bauxite, No. 69	Phosphoric	1.26	...	0.426	0.420

^a These samples contain nearly 30 mg. of manganese.

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Volumetric and Gravitimetric Determination of Mercury as Periodate

Mercury may be quantitatively precipitated as mercuric periodate, $\text{Hg}_5(\text{IO}_6)_2$, from 0.15 *N* nitric or 0.1 *N* sulfuric acid solution. It may be weighed in this form, or determined volumetrically by iodometric methods. Moderate amounts of aluminum, cadmium, zinc, copper, nickel, calcium, and magnesium do not interfere.

MERCURIC periodate was first prepared in 1834 by Bengieser (2) by the action of sodium periodate on mercuric nitrate. Later it was prepared by Lautsch (6) and by Rammelsberg (7) who treated mercuric oxide with a nitric acid solution of periodic acid. It was described as an orange-red salt having the composition $\text{Hg}_5(\text{IO}_6)_2$, not decomposed at 100° C., but completely volatile on ignition. It was insoluble in water.

In the course of an investigation on periodates this salt was studied, particularly with reference to its suitability for the quantitative determination of mercury.

Experimental Data

Mercuric nitrate, dissolved in nitric acid of varying concentrations, was precipitated by the addition of excess of sodium periodate. Precipitation was complete at concen-

trations not greater than 0.15 *N*. At 100° C. the salt was appreciably soluble in water, but below 50° C. the solubility was practically negligible.

A sample of the salt was thoroughly washed with hot water, dried at 100° C. for 4 hours, and analyzed gravimetrically for iodine and mercury. It was dissolved in dilute nitric acid, tartaric acid was added, and the solution made ammoniacal. A slight excess of sulfite was added to reduce the periodate and the mercury was precipitated from the hot ammoniacal solution by hydrogen sulfide. After standing one hour, the mercuric sulfide was filtered through a filtering crucible with porous porcelain bottom, washed with hot water containing a little hydrogen sulfide, then with pure water, dried 2 hours at 100° C., and weighed. The filtrate was oxidized to sulfate by pure hydrogen peroxide, the excess removed by boiling, a little arsenite added to reduce any iodate, and after acidifying with nitric acid, the iodide was precipitated and weighed as silver iodide. The results were: found, 74.75, 74.73, 74.76 per cent of HgO, average 74.75 per cent, which is the theoretical value; 25.30, 25.26 per cent of I₂O₇, average 25.28 per cent, theory 25.25 per cent. The salt is thus shown to be the pentamercuric paraperiodate, Hg₅(IO₆)₂.

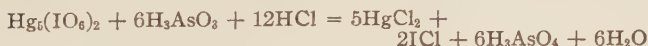
Some of this salt was recrystallized by dissolving it in concentrated nitric acid and diluting with water. The bright red crystals were washed and dried. They proved to be less pure than the precipitated salt. Analysis showed 73.83, 73.50, 73.76, 73.90 per cent of HgO, average 73.75 per cent, compared with the theoretical 74.75 per cent; and 25.26, 25.38, 25.30, 25.28 per cent of I₂O₇, average 25.30 per cent, compared with 25.25 per cent.

The iodine in mercuric periodate was determined volumetrically in two ways:

Method A—The salt was dissolved in excess of potassium iodide, acidified with hydrochloric acid, and the liberated iodine titrated with thiosulfate:



Method B—The salt was dissolved in an excess of standard arsenite by adding considerable concentrated hydrochloric acid, and the excess was titrated back with iodate using a little chloroform as indicator (1, 5):



In six titrations of the precipitated salt by these methods the maximum variation from the theoretical value was only 0.02 per cent.

Quantitative Determination of Mercury

Mercury is usually weighed as metal or as mercuric sulfide. Precipitation of the latter in hydrochloric acid solution is

not entirely satisfactory (3), especially in the presence of zinc, cadmium, and copper, because of contamination with other sulfides. Volumetrically mercury may be determined in a number of ways, most of which are not particularly accurate, the thiocyanate titration (4) being a common and accurate one.

It has been found that mercury can be determined gravimetrically or volumetrically by precipitation as mercuric periodate, $\text{Hg}_5(\text{IO}_6)_2$, in the presence of aluminum, zinc, cadmium, nickel, copper, calcium, and magnesium. The method is rapid, convenient, and accurate, and the end point in the volumetric method is very sharp. Iron interferes because it is precipitated as ferric periodate. Attempts were made to keep it in solution as the complex fluoride, but under these conditions the mercury was not completely precipitated. Chloride and other halides must be absent, because they prevent complete precipitation of mercury, doubtless owing to the slight ionization of mercuric halides. The maximum permissible acidity for complete precipitation is 0.15 *N* nitric or 0.1 *N* sulfuric acid, and under these conditions a large excess of periodate is required.

Table I—Gravimetric Determination of Mercury as $\text{Hg}_5(\text{IO}_6)_2$

MERCURY		ERROR	ACID PRESENT
Taken Gram	Found Gram		
0.0497	0.0497	0	Nitric
0.1243	0.1240	— 0.3	Nitric
0.1563	0.1563	0	Nitric
0.2904	0.2903	— 0.1	Nitric
0.3882	0.3885	+ 0.3	Nitric
0.5493	0.5492	— 0.1	Nitric
0.5721	0.5721	0	Nitric
0.4799	0.4798	— 0.1	Sulfuric
0.6313	0.6311	— 0.2	Sulfuric
0.4852	0.2563	—228.9	Hydrochloric ^a

^a Effect of hydrochloric acid in preventing precipitation is shown.

PROCEDURE—A sample of pure mercury was dissolved in nitric acid, sp. gr. 1.2, and the solution evaporated to dryness. It was taken up with 150 cc. of 0.15 *N* nitric acid or 0.1 *N* sulfuric acid, heated to boiling, and the mercury precipitated by adding slowly, with constant stirring, 2 grams of sodium or potassium periodate dissolved in 50 cc. of water. It was cooled, filtered through a filtering crucible with a sintered-glass or porous porcelain bottom, washed with warm water, dried at 100° C. for 2 or 3 hours, and weighed as $\text{Hg}_5(\text{IO}_6)_2$. The results are shown in Table I.

Volumetric Determination

Method A—The filtered and washed precipitate of mercuric periodate in the crucible was treated with 2 or 3 grams of solid potassium iodide and 10 to 15 cc. of water, stirring until all the periodate had dissolved. The solution was washed into a 150-cc. conical flask (most conveniently a suction flask), acidified with 10 cc. of 2 *N* hydrochloric acid, and the liberated iodine titrated with 0.1 *N* sodium thiosulfate, using starch as indicator.

Method B—The precipitate in the crucible was treated with an excess of standard arsenite and then concentrated hydrochloric acid added until it dissolved, about 35 cc. being required if the volume at the end of the titration is about 100 cc. The solution was washed into a 150-cc. glass-stoppered conical flask, and titrated with 0.1 *N* potassium iodate until it had a light brown color. Four or five cubic centimeters of chloroform were then added and the titration continued, shaking after each addition until the purple color of the iodine just disappeared (1, 5). The solution at the end point should contain between 28 and 45 cc. of hydrochloric acid, sp. gr. 1.18, per 100 cc.

The results, both with pure mercury and in mixtures with other metals, are shown in Table II. In the first three experiments method *B* was used; in all others, method *A*. The mercuric salt was precipitated from a nitric acid solution.

Table II—Volumetric Determination of Mercury as $\text{Hg}_2(\text{IO}_6)_2$

MERCURY		OTHER METALS	
Taken	Found	PRESENT	ERROR
Gram	Gram	Gram	Mg.
0.3645	0.3646		+0.1
0.2071	0.2070		-0.1
0.0513	0.0513	0.20 Ni	0
0.2556	0.2558	0.15 Al	+0.2
0.1327	0.1327	0.18 Cd	0
0.1903	0.1902	0.17 Zn	-0.1
0.1064	0.1065	0.13 Cu	+0.1

If a chloride solution is to be analyzed, the mercury may first be precipitated as metal or sulfide and then converted into nitrate or sulfate.

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The Action of Periodate on Salts of Various Metals

Bismuth.—Bismuth was completely precipitated when a solution of its perchlorate in 0.3 *N* perchloric acid was treated with sodium periodate. The white bulky precipitate became dense upon boiling the solution in which it was suspended. It was found that bismuth could be quantitatively separated from silver but not from lead by precipitating it as the periodate. Its properties are, however, such as not to recommend it for quantitative work. It is of indefinite composition although it approximates most closely the formula $\text{Bi}_4\text{H}_3(\text{IO}_6)_3$. One hundred cc. of boiling water dissolved an amount equivalent to 0.04 mg. of bismuth.

Silver.—Silver is incompletely precipitated by adding sodium periodate to a neutral solution. The brown precipitate is completely soluble in 0.3 *N* nitric acid.

Cerium.—When a cold cerous sulfate solution 0.16 *N* with nitric acid was treated with sodium metaperiodate, bright orange crystals of ceric periodate formed after 12 hours. Boiling the solution hastened the oxidation of the cerium and its subsequent precipitation. The action of periodate on a ceric sulfate solution gave complete precipitation of the cerium, but the precipitate was of indefinite composition and showed such great adsorptive tendency that it was useless for quantitative work.

Titanium.—A solution of titanium sulfate containing sufficient sulfuric acid to keep the titanium in solution was unaffected by the addition of a periodate. The separation of cerium from titanium was unsuccessful because the titanium was adsorbed by the precipitated ceric periodate.

Zirconium.—When a solution of zirconium sulfate in 1 *N* sulfuric or 0.7 *N* nitric acid was treated with sodium periodate, complete precipitation of the zirconium occurred. The white voluminous zirconium periodate did not become crystalline upon boiling the solution in which it was suspended. Attempts to use it as the basis of quantitative separation were unsuccessful for the reasons given under "Cerium."

Thorium.—When thorium nitrate was dissolved in 0.16 *N* nitric acid and treated with sodium periodate the thorium was completely precipitated as a white voluminous periodate which did not become crystalline.

Thallium.—A chocolate-brown voluminous precipitate of thallic periodate was formed when a slightly acid thallic nitrate solution was treated with sodium periodate. Com-

plete precipitation occurred when sufficient time was allowed for the oxidation of the univalent thallium which, as such, was not precipitated. The composition of the precipitate was not sufficiently definite for quantitative work.

Rare Earths.—Yttrium, lanthanum and praseodymium were completely precipitated as white, gelatinous periodates when neutral solutions of their nitrates were treated with sodium periodate. The addition of 0.2 cc. concentrated nitric acid dissolved the precipitates. This is typical of the action on salts of the rare earths.

Chromium and Vanadium.—Chromic salts are completely oxidized to chromic acid in neutral solution but incompletely in 0.2 N sulfuric acid. Vanadium is completely oxidized in 2 N sulfuric acid or in 4.5 N phosphoric acid.

Cobalt.—Small green crystals of cobaltic periodate formed when a cobaltous nitrate solution was treated with a periodate, but under conditions for its complete precipitation a separation from nickel was not possible.

Iron.—Iron was completely precipitated as a yellow salt from a slightly acid solution when treated with sodium periodate.

Barium and Strontium.—A slightly acid solution of barium nitrate when treated with sodium periodate did not give a precipitate until it was stirred, then almost complete precipitation of white crystalline barium periodate occurred. Strontium behaved like barium.

Metals not Precipitated.—Slightly acidified solutions of the following metals gave no precipitate when treated with sodium periodate: Beryllium, palladium, platinum, uranium, calcium, magnesium, aluminum, zinc, nickel, copper and cadmium. In slightly alkaline solution practically all metals form gelatinous precipitates.

SUMMARY

In alkaline solution practically all metals are precipitated by the addition of a soluble periodate. In slightly acid solution beryllium, palladium, platinum, uranium, calcium, magnesium, zinc, nickel, copper, cadmium, and aluminum are not precipitated.

Cerous, thallous, cobalt, chromium, vanadium and manganese salts are oxidized.

